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SEASONAL VARIATION OF POLYCHLORINATED BIPHENYL CONGENERS IN SURFICIAL SEDIMENT, TRAPPED SETTLING MATERIAL, AND SUSPENDED PARTICULATE MATERIAL IN LAKE MICHIGAN, USA

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Abstract—A unique time series of surface sediment, trapped settling material, and suspended particulate material polychlorinated biphenyl (PCB) samples were collected at a 45-m deep site off Grand Haven (MI, USA) over a 14-month period. Both concentrations and congener distributions remained constant for the sediments, although there were seasonal and interannual variability in the other matrices. Trapped settling material and suspended particulate material PCB concentrations were substantially lower (~50%) in 1997 than in the samples from December 1997 through July 1998. The cause could not be determined from the data collected, but there were some very large storms during the winter–spring period of 1998, resulting in major sediment resuspension throughout the southern basin. Observed seasonal variation in PCB concentration and congener distribution on particles likely was due to the changes in particle composition. These include particle size and the source of particles (such as the amount of resuspended sediment in trapped settling material), and the role of diagenesis of the organic matter on particles.

Keywords—Polychlorinated biphenyls   Sediment   Traps   Seasonal variation   Lake Michigan

INTRODUCTION

Polychlorinated biphenyl (PCB) manufacture and most uses were banned in North America in 1979, but interest has continued because PCBs can cause chronic harm [1]. The residence time of these hydrophobic organic contaminants in the Great Lakes is primarily controlled by the fate of particulate matter [2] due to partitioning to particles. The sediment organic carbon (OC) content largely controls sorption for persistent nonpolar organic contaminants [3]. Under equilibrium conditions, this OC partitioning (K_{OC}) is approximately equal to the contaminant's degree of hydrophobicity, represented by the octanol:water partition coefficient (K_{OW}). However, laboratory and field studies have demonstrated variable results regarding contaminant partitioning to sediments even when normalized to the OC content of the sediment [4–7]. Factors, which may contribute to the variance, include colloid influences, sorption kinetics, sediment characteristics, and the amount and type of black carbon [8,9].

Particle formation in Lake Michigan largely is driven by bluff erosion (~66% of new particulate material) with tributary and aeolian particulate matter contributing approximately 12% each [10]. Smaller, but important, amounts of transient particulate matter (organic matter, biogenic silica, and $CaCO_3$) are produced via primary production. Over long time scales (years), particulate material and associated constituents are transferred from the water column to the sediments. In-lake mixing processes and local bioturbation combine to create a sediment reservoir representing decades of inputs available for exchange through resuspension and biological pathways. The average Lake Michigan time constant (the mixed depth divided by the depositional rate) for particle removal is approximately 20 years [10].

Large episodic events resuspend, sort, and transport particles and associated contaminants from temporary sinks to more permanent sinks with a small fraction becoming incorporated into the sediments annually. During these resuspension events, there is an opportunity for the lake to reequilibrate with the constituents in the resuspendable sediment pool representing years to decades of constituent loading. Sediment–water exchange can occur in either direction with particles either scavenging or desorbing water column contaminants.

Desorption studies have demonstrated that contaminant–particle partitioning kinetics show hysteresis, with desorption rates slower than adsorption rates [11]. Based on these findings and the physics of the system, there can be a decoupling of the contaminant concentration on particles from that observed dissolved in the water column. For instance, the sediments in depositional basins within the Great Lakes often exhibit high contaminant and radiotracer concentrations [12–14]. This focusing of contaminants results from movement of particles primarily during large resuspension events, or plumes [10]. Great Lakes field data have shown PCB and polycyclic aromatic hydrocarbons partitioning for seasonal plumes exhibiting both nonequilibrium and equilibrium conditions with dissolved concentration depending on the particular event. For Instance, PCB partitioning in a large plume event in southern Lake Michigan in 1998 was poorly correlated to K_{OW} [15]. The PCB concentrations of material settling into the sediment traps deployed in Lake Ontario (North America) decreased during resuspension events relative to the other sampling periods [16], suggesting that the source of material to the traps was depleted in PCBs. However, some southern Lake Michigan nearshore sites trapped settling material (TSM) and sediment samples had relatively higher PCB concentrations than off-
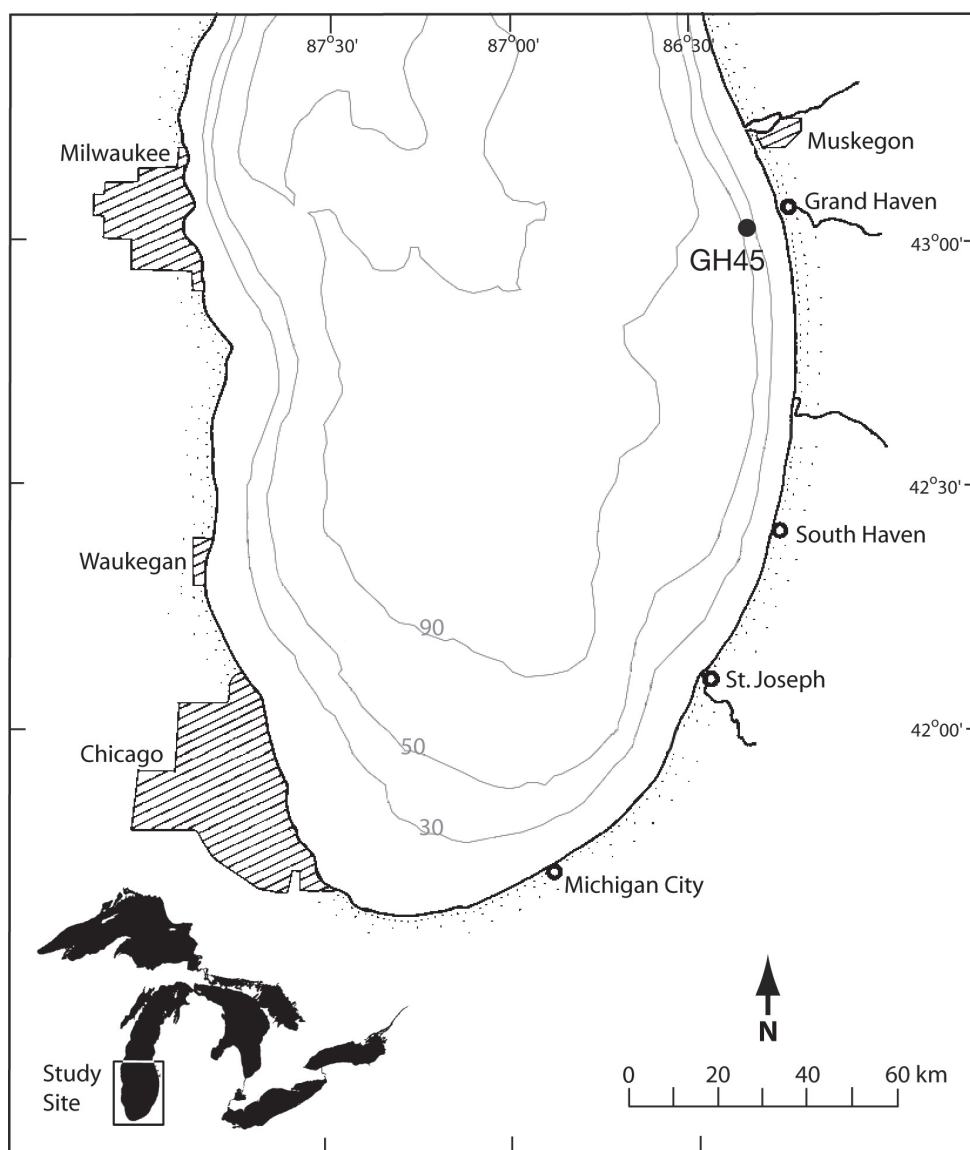
Fig. 1. Map of southern Lake Michigan, USA. Samples described were collected at station GH45.

shore samples [17]. The nearshore sediments and TSM samples were enriched in lower chlorinated PCBs, although sediments and TSM from deeper stations had elevated concentrations of more highly chlorinated PCBs.

In addition to differences in the equilibrium state for suspended particulate material (SPM), there is evidence of the impact of decomposing organic matter releasing contaminants such as PCB as a result of recycling in the benthic region [18]. All of these features, including variation in the PCB source function such as atmospheric deposition to the Great Lakes [19], can result in variations in the partitioning behavior of contaminants in the sediments and the TSM. This partitioning is critical for the transport and congener composition of PCB to the sediments where such materials ultimately serve as a contaminant source to the benthic community. It currently is well recognized that sediment-associated contaminants act as an important source to the food web and keep the food web concentrations elevated in persistent contaminants such as PCB [20,21].

The objective of the present study was to examine the seasonal variation in PCB concentrations and congener distri-

butions in SPM, TSM, and surficial sediments that serve as a potential source of PCB contamination to the benthic community in Lake Michigan.

MATERIALS AND METHODS

Sample collection

Surficial sediment, TSM, and near-bottom water (SPM) samples were collected approximately monthly during 1997 and 1998 from Lake Michigan off Grand Haven (MI, USA; 43°2.5′N, 86°20.0′W) at a 45-m deep site (Fig. 1). Temperature (°C) and light transmittance were measured throughout the water column using a SBE 19 Seacat Conductivity, Temperature, and Depth Profiler (Sea Bird, Bellevue, WA, USA) at the time of collection.

Sediment was collected using a stainless steel Ponar grab from April to December 1997 and March to June 1998. November collections were not made due to unfavorable weather conditions. The top 1 to 2 cm of sediment was removed using a stainless steel spatula and transferred to solvent-rinsed glass jars. (This depth likely represents more than a decade of ac-

cumulated particles. See *Discussion* section below). Samples were placed on ice for transport to the laboratory. Sediment samples were frozen at −15°C until analysis.

Trapped settling material was collected using sequencing sediment traps [22,23] deployed at 30 m from April to October 1997. The thermocline during the stratified period ranged from 15- to 25-m depth. The traps were set at 30 m to ensure that they would reflect the particles available for settling to the sediment. Twenty-three independently programmable 60-ml bottles rotated sequentially for a period of 9 d each to collect settling particles. Trapped settling material samples were preserved with 6 mg of HgCl2 to prevent bacterial decomposition [24]. For the 1998 season, 10.2-cm diameter nonsequencing traps, preserved with 6 ml of chloroform [24], were deployed and retrieved at this same depth on approximately a monthly basis from March to June because the sequencing traps were not available. The two types of traps have been intercalibrated and show no biases in the collection of TSM [22]. Studies at our laboratory and in the field [25] showed no difference in the homolog distribution when using either of the two metabolic poisons. At the laboratory, the wet TSM samples were passed through a 0.5-mm screen to remove large debris and zooplankton, and carefully split in half ([26] http://www.epa.gov/glnpo/lmmb/methods/spliter.pdf), with one-half freeze-dried for the determination of dry weight, particulate mass flux, organic carbon content, and biogenic silica. The other half of the sample was stored frozen for PCB analysis. The biogenic silica (SiO2) content was determined using a wet alkaline digestion with 1% Na2CO3 at 85°C [27]. Mineral contributions to the silica pool were corrected using a timed extraction procedure to distinguish the differential rates of extraction for biogenic versus mineral forms [28].

Prior to the field collection of SPM samples, particulate organic carbon (POC) filters (25-mm diameter type A/E glass fiber filters, Gelman Sciences, Ann Arbor, MI, USA) were ashed at 450°C for 4 h and desiccated until use. The filtering apparatus and glassware for POC analysis were rinsed with 1 N HCL. For total suspended solids (TSS), glass fiber filters (47 mm) were rinsed with deionized water, dried overnight, weighed, and placed in a dessicator until use. A 20-L glass carboy to collect water for particulate PCB, POC, and TSS analysis was washed with soap and water and then rinsed with pesticide-grade acetone and distilled water. Glass fiber filters (293-mm diameter, Gelman Sciences) for the particle-associated PCB were solvent-rinsed (three times) with pesticide-grade acetone and subsequently rinsed (three times) with methylene chloride. All stainless steel tubing in the filtration system was rinsed with acetone and deionized water.

Water samples for SPM were collected in June, August, and December 1997 and May and June 1998. For each collection, a cleaned Niskin℠ (General Oceanics, Miami, FL, USA) bottle was used to collect water in the benthic-nephloid region located approximately 2 m above the bottom sediment. Duplicate water samples were taken during the August 1997 sample collection. At the laboratory, quality control samples, including blank filters, were stored along with the field samples. Approximately 100 L of water, under nitrogen gas pressure, was passed through a large glass fiber filter. Backpressure was monitored and the flow rate was maintained at approximately 220 ml/min. Each sample required approximately 7 to 8 h to process. During this time, samples for TSS and POC were prepared from the separate water collection by vacuum filtration. Volumes filtered to measure TSS and POC ranged

from 2 to7 L and 200 to 600 ml, respectively, depending on the amount of solids needed to drastically reduce the flow-through of filtrate. All samples for TSS, POC, and PCB analysis were frozen at −15°C prior to analysis.

The amount of suspended solids in a whole water sample was determined by drying and weighing the TSS-laden filters and calculating the mass per liter filtered. Control TSS filters were weighed alongside the sample filters to account for changes in mass due to environmental conditions, such as humidity. The average coefficient of variation for triplicate samples in the present study was 2.3%.

Sample extractions and clean up

The extraction and cleanup procedures generally followed those outlined by Van Hoof and Hsieh ([29]; http://www.epa.gov/glnpo/lmmb/methods/sop-401.pdf). All materials were cleaned by either soap and water washing and solvent rinsing or by ashing at 450°C for 4 h.

After sediment samples were thawed at 4°C, 30 g of each was taken for PCB extraction. Three subsamples from each sediment sample also were weighed. These subsamples were dried at 60°C and reweighed for dry- to wet-weight ratios. Finally, subsamples also were taken for OC analysis. These subsamples were freeze dried, acidified with 2N HCl, shaken overnight to remove carbonates, oven dried at 70°C, reground, and stored in a dessicator until analysis.

The 30 g of sediment was mixed with ashed sodium sulfate to remove excess water prior to the addition of 150 ml methylene chloride and PCB surrogate standards (congeners 14, 65, 166; Ultra Scientific, North Kingstown, RI, USA) used for contaminant recovery measures. Samples were sonicated at 60 Hz (Branson model 8210 ultrasonic water bath, Danbury, CT, USA) and 30°C for 1 h. Extracts were allowed to equilibrate for 22 h at 30°C, followed by sonication for an additional hour. After filtration through glass wool, extracts were concentrated on a Kadurna-Danish solvent evaporator system (Organomation, Berlin, MA, USA) to 10 ml, followed by nitrogen gas volume reduction to 1 ml. Methylene chloride was then solvent exchanged with hexane prior to sample clean up.

The TSM sample extraction procedures were identical to sediment procedures. However, the water in the trap bottles was removed and extracted separately with 150 ml methylene chloride. The same methylene chloride was used to extract the sodium sulfate–dried detritus. Some of the temporally adjacent 9-d TSM samples were combined. Compositing the small TSM samples was necessary to ensure reliable analysis above the limit of detection (see below).

Methods for the extraction of SPM on filters were based on those of Marti and Armstrong [30]. Filters were soxhlet extracted with acetone:hexane (60:40, v/v) for 24 h. The extracts were then back extracted into hexane using deionized water to remove the acetone and concentrated as above.

All extracts were cleaned up on columns containing 10% deactivated alumina and 3% deactivated silica. Polychlorinated biphenyls were eluted from the column with 35 ml hexane. The PCB column fraction was reduced by nitrogen evaporation to 1 ml and then spiked with internal standards (PCB congeners 30 and 204, Ultra Scientific for gas chromatography analysis).

Clean PCB extracts from sediment were treated with activated copper to remove sulfur. Copper was activated by exposure to concentrated HCl. Sulfur was considered completely removed once added copper no longer turned dull.

Quality control samples included laboratory reagent blanks

Table 1. Relative percent difference (RPD) and method detection limit (MDL) for congeners from each matrix that passed quality control

IUPAC[c] no.	Log K_{OW}[d]	Sediment[a]		TSM[b]		SPM[a]	
		RPD (%)	MDL (ng)	RPD (%)	MDL (ng)	RPD (%)	MDL (ng)
18	5.24	17.1	0.13	17.1	0.13	10	0.13
15+17	5.28	16.3	0.29	—	—	—	—
32	5.44	33.5	0.19	—	—	—	—
45	5.53	55.1	0.10	—	—	—	—
22	5.58	13.5	0.29	13.5	0.29	—	—
53	5.62	23.2	0.09	—	—	—	—
26	5.66	20.2	0.19	—	—	—	—
31+28	5.67	17.8	0.28	17.8	0.28	2	0.24
25	5.67	25.5	0.17	—	—	—	—
52	5.84	22.2	0.14	22.2	0.14	12	0.14
56+60	6.11	17.3	0.19	17.3	0.19	1	0.15
70+76	6.16	22	0.13	22	0.13	4	0.11
66	6.2	19.3	0.24	19.3	0.24	2	0.20
92+84	6.2	16.2	0.18	16.2	0.18	16	0.18
74	6.2	20.7	0.14	20.7	0.14	2	0.12
82	6.2	8.3	0.12	—	—	—	—
136	6.22	20.3	0.11	—	—	—	—
85	6.3	21.6	0.13	21.6	0.13	10	0.12
101	6.38	26.4	0.15	26.4	0.15	24	0.10
110	6.48	18.7	0.12	18.7	0.12	19	0.10
151	6.64	21.4	0.11	—	—	—	—
135+144	6.65	24.6	0.15	—	—	—	—
123+149	6.7	18.9	0.10	18.9	0.10	37	0.09
107	6.71	16.1	0.17	—	—	—	—
118	6.74	17.4	0.16	17.4	0.16	21	0.13
128	6.74	12.6	0.09	—	—	—	—
141	6.82	21.8	0.07	—	—	—	—
158	7.02	19.4	0.17	—	—	—	—
177	7.08	22.9	0.13	—	—	—	—
174	7.11	23.7	0.12	—	—	—	—
178	7.14	33.8	0.16	—	—	—	—
202+171	7.17	17.9	0.09	—	—	—	—
187+182	7.18	26.6	0.10	26.6	0.10	20	0.09
156	7.18	22.2	0.09	—	—	—	—
183	7.2	24.5	0.13	—	—	—	—
172	7.33	27	0.18	—	—	—	—
170+190	7.35	23	0.14	—	—	—	—
180	7.36	24.8	0.15	24.8	0.15	16	0.13
194	7.8	28.2	0.13	—	—	—	—

[a] The only congeners listed are those that passed quality control. SPM = suspended particulate material.
[b] TSM = trap settling material. The RPD and MDL are the same as for sediment and show those congeners that passed quality control.
[c] IUPAC = International Union of Pure and Applied Chemistry.
[d] Log K_{OW} = octanol–water partition coefficient.

that contained 7 to 80 g of sodium sulfate, depending on the water content of a particular matrix. They also included field blanks, laboratory and field duplicates, and matrix-spike samples. These samples were treated the same as the unknowns. The matrix samples included down-core, preindustrial sediment that was fortified with target analytes used to determine which surrogates would correct the data. Except for congener 18, all field and lab blanks were less than 10% of the average congener concentration for SPM and less than 3% for TSM and sediments. Total PCB blanks were less than 3% for all samples. Consequently, none of the reported data have been blank corrected except for congener 18.

PCB and organic carbon analyses

Polychlorinated biphenyl analyses generally followed Van Hoof and Hsieh ([31]; http://www.epa.gov/glnpo/lmmb/methods/sop-501.pdf). Clean samples were run on a Hewlett-Packard model 5890 gas chromatograph equipped with a ^{63}Ni electron capture detector, splitless injector, autosampler (Agilent Technologies, Wilmington, DE, USA), and a DB-5 60-m × 0.25-mm (internal diameter) fused silica capillary

column with a 0.1-μm film thickness (J&W Scientific, Folsom, CA, USA). The oven temperature program was as follows: 100°C at 0 min, 100 to 265°C at 1°C/min, and 265 to 300°C at 20°C/min.

Congeners were quantified using multilevel calibration solutions of a mixed Arochlor standard (M. Mullin, U.S. Environmental Protection Agency, Grosse Ile, MI, unpublished data). Polychlorinated biphenyls standard recoveries averaged 96.1%. Surrogate correction was performed using PCB congener 65 (Ultra Scientific). Recoveries of this surrogate ranged from 64 to 112%, with a mean of 83%. Data were flagged when preset criteria were not met, including surrogate and matrix spike recoveries that fell outside the range of 50 to 130%, sample and duplicate relative percent differences that exceeded 30% when the congener mass was >five times the method detection limit (MDL) or exceeded 50% if the peak was smaller, peak masses that fell below the MDLs (see Table 1), and blank congener levels that exceeded MDLs.

Method detection limits were determined on preindustrial sediment. Bottom sediment MDLs were used for TSM and SPM detection limits as well. For MDL determinations, ap-

Table 2. Sample characteristics and suspended particulate material polychlorinated biphenyl (PCB) concentrations (ng/g dry wt)

Month collected	June 1997	Aug. 1997	Dec. 1997	May 1998	July 1998	Avg. (ng/g)	Avg. blank (%)
Organic carbon (%)	14.4 ± 0.5	15.1 ± 0.3	12.2 ± 0.2	13.5 ± 0.3	9.5 ± 0.1	—	—
IUPAC[a] no.							
18	0.97	1.27	2.04	2.31	1.48	1.6	36.1
31+28	5.73	5.98	6.56	6.37	5.54	6.0	14.6
52	2.48	3.17	3.67	4.85	4.99	3.8	9.3
56+60	3.00	2.56	2.92	2.89	2.79	2.8	8.8
70+76	3.07	3.05	3.20	3.45	2.96	3.1	5.9
66	5.85	5.34	5.24	5.59	5.34	5.5	1.1
92+84	2.05	2.27	4.00	4.00	2.28	2.9	5.4
74	1.55	1.35	1.47	1.67	1.30	1.5	1.0
85	1.03	0.98	5.71	4.42	1.16	2.7	0.9
101	2.28	2.82	4.01	4.23	2.66	3.2	4.2
110	3.82	4.07	5.90	5.76	4.02	4.7	3.1
123+149	1.26	1.61	3.99	3.78	2.08	2.5	2.4
118	3.04	3.08	4.46	4.11	3.39	3.6	2.9
187+182	0.73	0.95	6.08	6.31	2.83	3.4	2.2
180	1.56	1.94	5.63	5.84	3.61	3.7	0.5
Total PCB (ng/g)	38.40	40.45	64.88	65.59	46.41	51.1	—
Total blank/total sample (%)	2.70	7.38	7.66	4.66	6.54	—	—
TSM[b] (mg/L)	3.40	1.64	1.10	1.60	1.88	—	—
Volume filtered (L)	77.82	75.82	78.75	83.1	77.18	—	—

[a] IUPAC = International Union of Pure and Applied Chemistry.
[b] TSM = total suspended matter.

proximately 0.2 to 2 ng of each of 10 congeners (one selected from each homolog group) were spiked onto several sediment samples. Method detection limits for each of the 10 congeners were calculated by multiplying the standard deviation of the replicates by the one-tailed *t* statistic at a 99% confidence level for the number of replicates measured. Normally, the MDL of the congener that represented a homolog group was used for all of the congeners in that group. However, due to the range of responsiveness of congeners within any particular homolog group, the representative congener with the largest MDL statistic (a) was used to derive MDLs for all of the remaining congeners in the homolog group (b; Eqn. 1).

$$\text{Derived MDL(b)} = \text{MDL(a)} \times (\text{RRF[a]}/\text{RRF[b]}) \quad (1)$$

Therefore, the greater the detector response for a congener (b), the lower the derived MDL could be relative to the known MDL (a) and corrected for the relative response factor (RRF) of the two compounds.

Organic carbon analyses for sediment, TSM, and SPM were performed using two carbon, hydrogen, nitrogen analyzers, a Perkin Elmer model 2400 (Perkin Elmer, Norwalk, CT, USA), or a model EA 1110 from CE Instruments (ThermoQuest Italia, Milan, Italy). In-house standards from sites with comparable percent organic carbon were used to create calibration curves. These standards and National Institute of Standards and Technology certified standards were run with the samples. All standards fell within the acceptable range of values (average ± 1 standard deviation) and compared well between instruments. Analysis of blank filters resulted in values never greater than 3% of the POC samples. Results were not blank corrected.

PCB selection

Only the congeners that passed MDL and blank tests were used in this report. Because of ambient concentrations and sample size restriction, there were different numbers of congeners for each of the three sample types. Sediments had the most congeners (39), followed by TSM (16), and then SPM

(15). The congeners common to all three matrices covered a range of log K_{OW} (5.24–7.36 [31]; http://www.epa.gov/glnpo/lmmb/methods/sop-501.pdf). The congeners that did not survive the quality assurance/quality control test as we progress from sediments to water, generally were lowest in ambient concentration. Thus, in the sediment samples, the sum of the 15 congeners accepted in the SPM samples comprise an average of 80% of the total 39 congeners that passed quality assurance/quality control criteria for sediments.

RESULTS

Total PCBs

A summary of all congener data is presented in Tables 1 to 4, and total PCB in the three sample matrices are shown in Figure 2. Variability in analyses of each matrix was evaluated by examining the relative percent differences (RPDs = 100 × absolute difference/average) for surface sediment, and SPM field duplicates (Table 1). Trapped settling material sample duplicates were not available. Additionally, there were nine field replicates of surface sediments (separate cores) analyzed as part of the Lake Michigan mass balance program using the identical procedures [29,31]. These data were combined with the few RPDs specifically measured in this study and used as the RPD for sediments. Relative percent differences for the 39 congeners in field duplicates of sediments ranged from 8.3 to 55.1% and averaged 22.2%.)

Suspended particulate material PCBs

The concentration of SPM was highest for the June 1997 sampling period (3.4 mg/L). The remaining four collections had values ranging from 1.1 to 1.9 mg/L (Table 2). The organic carbon concentration of these samples ranged from 9.5 to 15.1%, but did not exhibit a seasonal pattern. Total PCB concentrations ranged from 38.4 to 65.6 ng/g and were highest for the two samples collected during the unstratified period (Fig. 2). The most abundant congener was the unresolved pair 31+28.

Table 3. Sample characteristics and trapped settling material polychlorinated biphenyl concentrations (ng/g dry wt)

Collection date	Apr. 9–18, 1997	May 15–24, 1997	May 24–Jun. 20, 1997	Jun. 20–Jul. 8, 1997	Jul. 8–Aug. 4, 1997	Sept. 18–Oct. 6, 1997	Mar. 3–Apr. 1, 1998	Apr. 6–May 17, 1998	May 18–Jun. 19, 1998		
Sample ID no.	T1	T2	T3	T4	T5	T8	T9	T10	T11		
Dry weight (g)	4.10	0.90	0.36	0.57	0.57	0.63	13.88	2.88	0.64		
Mass flux (g/m²/d)	16.61	8.68	1.15	0.86	0.82	6.29	33	5.06	1.14		
Organic carbon (%)	2.28	2.56	4.28	4.28	5.34	3.13	1.79	2.73	5.09		
Biogenic SiO2 (mg/g)	74.12	30.12	60.13	118.23	—	—	—	—	—		
IUPAC[a] no.										Average	Average blank %
18	0.58	0.73	0.98	—	0.49	0.34	1.08	2.78	0.77	1.0	8.8
22	0.95	1.12	1.35	1.42	0.72	0.97	—	4.54	3.61	1.8	7.4
31+28	4.42	4.82	4.68	4.91	2.74	2.89	6.94	16.86	17.52	7.3	0.8
52	1.50	1.60	1.62	1.97	0.81	1.93	1.63	4.41	6.16	2.4	0.0
56+60	2.04	1.82	1.66	1.63	0.90	1.22	—	2.75	3.68	2.0	0.9
70+76	2.09	2.05	2.09	2.13	1.15	1.79	1.71	2.75	3.48	2.1	3.4
66	4.19	3.85	3.44	3.61	2.04	2.38	3.47	4.52		3.4	0.6
92+84	1.55	1.35	1.69	1.84	0.84	3.10	1.42	2.57	3.64	2.0	0.5
74	1.10	1.03	0.96	0.99	0.55	0.74	0.93	1.51	1.69	1.1	0.5
85	0.60	0.57	0.64	0.62	0.31	0.90	0.61	0.81	1.22	0.7	0.3
101	1.38	1.31	1.54	1.80	0.84	3.14	1.25	2.83	4.59	2.1	0.4
110	2.45	2.26	2.49	2.83	1.41	4.44	2.21	3.09	5.32	2.9	0.3
123+149	0.61	0.59	0.81	0.96	0.41	1.20	0.57	1.11	1.80	0.9	0.3
118	1.67	1.58	1.79	1.74	0.97	2.01	1.57	2.04	3.41	1.9	0.9
187+182	0.33	0.30	0.44	0.58	0.21	0.37	—	0.47	0.83	0.4	1.0
180	0.90	0.81	1.05	1.43	0.54	1.02	0.76	0.91	1.74	1.0	1.0
Total (16)[b] (ng)	26.35	25.79	27.22	28.47	14.92	28.45	24.14	53.97	59.47	25.1	32.1
Total (15)[b] (ng)	25.40	24.67	25.87	27.05	14.20	27.48	24.14	49.43	55.86	24.1	30.5

[a] IUPAC = International Union of Pure and Applied Chemistry.
[b] The 16 and 15 refer to all the congeners that passed quality control for trapped material and suspended particle, respectively.

Trapped settling material and sediment PCB

Trapped settling material mass fluxes exhibited the seasonal pattern seen throughout the Great Lakes, with high flux values during the unstratified period, declining to much smaller values once the lake became stratified (Fig. 2). Fluxes range over a factor of 10 or more. The OC in the TSM samples averaged less than 30% of the organic carbon in the SPM. The TSM represents a mixture of settling SPM and resuspended sediment. The SPM has a range of apparent settling velocities, and the fraction of trapped settling material from SPM may have some compositional differences due to this sorting process. The other component of TSM, resuspended sediment, may be represented differently in the SPM samples. This component would be sampled by the trap throughout the trap sampling interval when materials either are locally resuspended primarily by waves or transported from other areas where resuspension has occurred. Biogenic silica was measured on TSM and exhibited a strong seasonal cycle (Table 3). Highest concentrations are due to the settling (and subsequent resuspension) of diatoms; these samples also have the highest concentrations of organic carbon.

The PCBs in trapped settling materials had concentrations generally lower than in the suspended particulate material. Again the congener pair 31+28 appeared in highest concentration. Except for the last two trapped settling material samples, the total PCB in the trapped settling material was only about one-half the concentration of the SPM. Counterintuitively, the trapped settling material with the highest OC (July to August 1997) had a substantially lower concentration of PCB than any other trapped settling material sample (Fig. 2). The last two trapped settling material samples, from the spring of 1998, had twice the concentration of PCB of the spring samples from 1997 and correspond to the period of high con-

centration in the SPM. Although relative percent differences could not be determined for PCBs from trapped settling material, they were expected to be similar to relative percent differences from surficial sediment (Table 1), because these two particle types were extracted and analyzed using essentially the same procedure.

The concentration of total PCB in surface sediments ranged from 6.1 to 10.8 ng/g for the 15 congeners common in all matrices. This increased to a range of 7.7 to 13.4 when all 39 congeners that passed our quality assurance/quality control were included (Table 4). The congener pair 31+28 and congener 66 were approximately equal and most abundant in the sediment samples. Considering the magnitudes of the congener-specific RPDs for the sediment replicates (Table 1), the temporal differences among the 13 sediment samples disappears. The coefficient of variation for the total PCBs across time for any of the three congener combinations (17.1–17.3%) is less than the concentration-weighted RPD for field replicates (19.8%). A concentration-weighted RPD is calculated as

$$\sum (C_i \times \mathrm{RPD}_i) \Big/ \sum C_i \qquad (2)$$

where C_i is the congener concentration, and RPD_i is the value of the congener-specific RPD (Table 1).

DISCUSSION

Although there have been temporal studies of PCBs in sediment traps [15,17,18], the resampling of TSM, SPM, and sediment from a single station over a 14-month period represents a unique window on the behavior of these compounds over relatively short time scales.

Sediments represent field replication at this site

Sediment data provide a unique perspective on the variability associated with resampling a single site; such repre-

Table 4. Sample characteristics and surficial sediment polychlorinated biphenyl concentration (ng/g dry wt)

Month collected	Apr. 1997	May 1997	Jun. 1997	Jul. 1997	Aug. 1997	Sep. 1997	Oct. 1997	Dec. 1997	Mar. 1998	Apr. 1998	May 1998	Jun. 1998	Avg.
Organic carbon (%)	0.69 ± 0.02	0.59 ± 0.02	0.66 ± 0.02	0.58 ± 0.01	0.52 ± 0.02	0.69 ± 0.04	0.76 ± 0.04	0.67 ± 0.02	0.64 ± 0.08	0.56 ± 0.002	0.69 ± 0.04	0.72 ± 0.03	
IUPAC[a] no.													
18	0.16	0.11	0.12	0.12	0.09	0.12	0.18	0.12	0.17	0.14	0.13	0.15	0.13
15+17	0.21	0.16	0.17	0.18	0.13	0.17	0.27	0.18	0.26	0.19	0.18	0.20	0.19
32	0.08	0.06	0.06	0.07	0.05	0.06	0.10	0.06	0.10	0.07	0.07	0.07	0.07
45	0.05	0.03	0.04	0.04	0.03	0.04	0.06	0.05	INT	0.05	0.04	0.05	0.04
22	0.29	0.25	0.24	0.30	0.23	0.29	0.41	0.26	0.41	0.27	0.28	0.29	0.29
53	0.04	0.02	0.03	0.03	0.02	0.03	0.04	0.03	0.03	0.03	0.03	0.04	0.03
26	0.10	0.09	0.08	0.10	0.08	0.10	0.15	0.09	0.13	0.09	0.10	0.10	0.10
31+28	1.26	1.02	1.14	1.36	1.06	1.34	1.86	1.21	1.79	1.26	1.25	1.35	1.32
25	0.06	0.05	0.05	0.05	0.05	0.05	0.08	0.06	0.06	0.06	0.05	0.06	0.06
52	0.60	0.38	0.48	0.49	0.37	0.49	0.66	0.49	0.59	0.50	0.46	0.57	0.51
56+60	0.70	0.50	0.62	0.64	0.53	0.67	0.91	0.68	0.82	0.69	0.62	0.74	0.68
70+76	0.65	0.45	0.55	0.58	0.47	0.60	0.82	0.60	0.77	0.59	0.57	0.66	0.61
66	1.31	0.91	1.17	1.21	1.00	1.25	1.73	1.27	1.58	1.27	1.22	1.42	1.28
92+84	0.58	0.41	0.51	0.51	0.42	0.54	0.69	0.53	0.65	0.51	0.48	0.53	0.53
74	0.34	0.25	0.30	0.32	0.26	0.33	0.45	0.33	0.43	0.32	0.31	0.36	0.33
82	0.11	0.07	0.09	0.08	0.07	0.08	0.12	0.09	0.11	0.10	0.07	0.10	0.09
136	0.06	0.03	0.05	0.04	0.03	0.04	0.06	0.04	0.05	0.04	0.04	0.04	0.04
85	0.25	0.15	0.21	0.20	0.16	0.20	0.26	0.22	0.24	0.23	0.18	0.24	0.21
101	0.57	0.35	0.44	0.44	0.36	0.46	0.58	0.47	0.52	0.46	0.41	0.51	0.46
110	1.01	0.63	0.84	0.81	0.66	0.83	1.04	0.90	0.94	0.88	0.72	0.98	0.85
151	0.09	0.05	0.07	0.07	0.05	0.06	0.09	0.07	0.08	0.08	0.06	0.07	0.07
135+144	0.11	0.07	0.08	0.08	0.07	0.08	0.11	0.08	0.10	0.09	0.08	0.08	0.08
123+149	0.32	0.20	0.25	0.23	0.19	0.22	0.31	0.25	0.28	0.25	0.22	0.25	0.25
107	0.09	0.07	0.07	0.08	0.08	0.08	0.11	0.07	0.10	0.08	0.07	0.07	0.08
118	0.69	0.46	0.56	0.56	0.49	0.56	0.81	0.62	0.77	0.63	0.58	0.60	0.61
128	0.09	0.07	0.07	0.08	0.07	0.08	0.11	0.08	0.10	0.08	0.08	0.08	0.08
141	0.10	0.07	0.08	0.08	0.06	0.07	0.10	0.08	0.10	0.09	0.07	0.08	0.08
158	0.09	0.06	0.06	0.07	0.06	0.07	0.09	0.07	0.08	0.07	0.06	0.07	0.07
177	0.09	0.06	0.07	0.07	0.06	0.07	0.10	0.08	0.09	0.08	0.07	0.08	0.07
174	0.14	0.08	0.10	0.10	0.08	0.10	0.13	0.11	0.12	0.11	0.10	0.11	0.10
178	0.04	0.03	0.03	0.03	0.03	0.03	0.04	0.03	0.04	0.03	0.04	0.03	0.03
202+171	0.04	0.03	0.03	0.04	0.03	0.04	0.05	0.03	0.04	0.04	0.03	0.03	0.04
187+182	0.13	0.08	0.10	0.10	0.08	0.10	0.14	0.11	0.12	0.11	0.10	0.11	0.11
156	0.04	0.03	0.03	0.04	0.04	0.04	0.06	0.03	0.05	0.04	0.04	0.03	0.04
183	0.07	0.05	0.05	0.06	0.05	0.06	0.08	0.06	0.07	0.06	0.06	0.06	0.06
172	0.03	0.03	0.03	0.03	0.03	0.03	0.04	0.03	0.04	0.03	0.03	0.03	0.03
170+190	0.18	0.10	0.13	0.12	0.10	0.12	0.17	0.14	0.15	0.15	0.12	0.15	0.14
180	0.32	0.20	0.24	0.24	0.20	0.25	0.32	0.26	0.23	0.26	0.24	0.27	0.25
194		0.05	0.06	0.06	0.05	0.06	0.08	0.07	0.07	0.06	0.06	0.07	0.06
Total (39)[b]	11.12	7.70	9.30	9.72	7.90	9.79	13.38	9.93	12.28	10.08	9.35	10.71	10.11
Total (16)[b]	9.19	6.35	7.75	8.12	6.59	8.24	11.17	8.31	10.30	8.38	7.79	9.03	8.43
Total (15)[b]	8.90	6.10	7.51	7.81	6.36	7.95	10.75	8.05	9.90	8.11	7.50	8.74	8.14
Total (39)[b] (blank/ sample) (%)	—	—	—	—	—	—	—	—	—	—	—	—	0.21
Total (16)[b] (blank/ sample) (%)	—	—	—	—	—	—	—	—	—	—	—	—	0.24
Total (15)[b] (blank/ sample) (%)	—	—	—	—	—	—	—	—	—	—	—	—	0.08

[a] IUPAC = International Union of Pure and Applied Chemistry.
[b] The 39, 16, and 15 refer to all the congeners that passed quality control for the sediment, trapped material, and suspended matter, respectively.
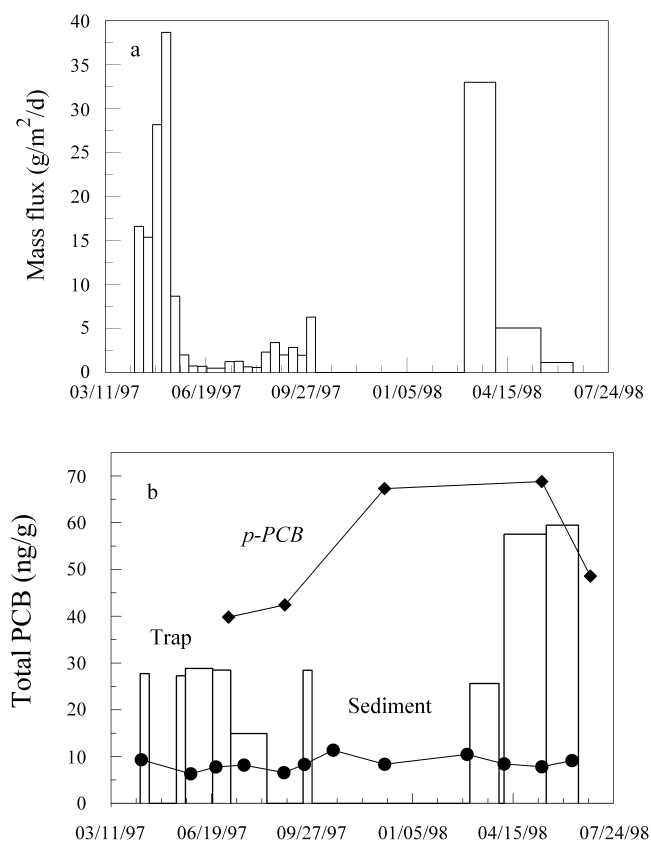
Fig. 2. Mass fluxes as measured in sediment traps (**a**). Seasonal concentrations for total polychlorinated biphenyls (PCBs) in sediments (●), trapped settling material (bars), and suspended particulate matter ([*p*-PCB], ◆) (**b**).
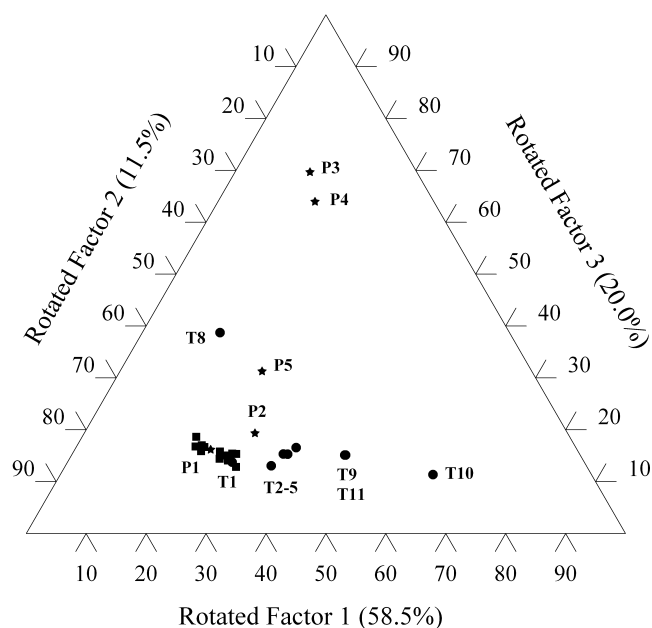

Fig. 3. Principle component analysis scores for the three major factors, totaling 91% of the overall variance in the data. The filled squares (■) represent the 11 individual sediment samples. The filled circles (●) T1 to T11 represent the eight trapped settling material samples. The stars (☆) represent the five suspended particulate material samples (see Table 1). PCB = polychlorinated biphenyl; PCA = principle component analysis.

sentativeness is always a concern. Because the concentration-weighted RPD for 12 sediment samples collected over 14 months was only slightly larger than the coefficient of variation for individual samples, the set of samples could be considered as a suite of field replicates, i.e., an estimate of how well individual samples represent this site.

No cores have been collected from this site for geochronology. Approximately 60% of the particles are between 64 and 200 μm, with only 10% less than 64 um [32]. It is difficult to collect and interpret radiochemistry in such sandy sediment. The nearest core collected and measured for geochronology is approximately 2.5 km to the southwest in 58 m of water, where over 50% of the sediment is less than 64 μm. This core had a measured accumulation rate of 0.08 g/cm²/year, a mixed layer equivalent to 13 years of accumulation (J. Robbins, Great Lakes Environmental Research Laboratory, Ann Arbor, MI, USA, personal communication), and the OC concentration at the surface was 1.7%, over twice the concentration of the 45-m-deep site (Table 4). The sandier conditions and the lower OC content suggest that this site does not accumulate particulate material as well as the station with the measured geochronology, and so the top 1 to 2 cm of sediment should represent a longer time frame of accumulation than that site. Thus, the mixed layer should represent more than 13 years of accumulation.

Although sampling with a Ponar grab sampler tends to blow away any surface floc material due to the bow wave associated with the device, this material represents a mixture of fine particles of different ages that are being reworked constantly into

the sediment, which can be resuspended during resuspension events. The loss of this fine material was not expected to greatly affect the comparison between sediments and the TSM or SPM as is suggested from the principal component analysis where several of the trapped settling material samples show the same congener distribution as the sediment (see *PCA results—congener distributions* section). The compositing in the upper 1 to 2 cm likely represents a mixed region probably greater than the 13 years measured further offshore. In addition, the grain size composition of surface sediment at this site is nearly constant for 2 to 3 km² [32]. Therefore the constancy of OC content, PCB concentration (Table 4), and congener distribution (Fig. 3) are not surprising and lead to the relatively constant RPD associated with resampling.

PCA results—congener distributions

Fifteen common congener data from all of the solids (sediment, TSM, and SPM) PCB data were subjected to a principle component analysis with varimax rotation. Principal component analysis is used to find a linear combination of variables with maximum variance. The variances associated with each component are calculated. In our case, the result was that three factors represented approximately 91% of the total variance from the original data correlations (Fig. 3). All 12 of the sediment samples map into a very small space, implying that, in addition to their constant concentration over the sampling period, their congener distributions are very similar. In all samples, congeners 31+28 or 66 had the highest concentration.

The congener distribution in TSM is more variable. The first collection (labeled T1 in Fig. 3 and Table 3) falls on top of a cluster of sediment values (Fig. 3), implying that the TSM had a large component of locally resuspended material. The higher concentration in the TSM likely is associated with size sorting during sediment resuspension, with the coarser sands

not diluting the TSM as much as the sediment. Trapped settling material samples T2 to T5 all plot together, somewhat removed from T1. The shift primarily is due to the fact that T1 has approximately 25% higher relative concentrations of congeners 56+60 and 66 than traps T2 toT5. This is comparable to the RPD values for the individual congeners for sediments (Table 4) and the RPD for TSM samples likely are at least as large due to the smaller sample size. Therefore, all of the sediments and TSM samples T1 to T5 are similar. Although sample T5 has only one-half the total PCB concentrations of any other sample, its congener distribution is similar to the other samples. Trapped settling material collections T6 and T7 (August 4–September 18) were not included in the analysis due to small sample size and the few congeners that passed quality assurance/quality control testing.

The location of TSM sample T8 on the PCA figure is quite different. This was the only TSM sample where congener 31+28 was not the major component, being only 65% of the major peak (congener 110). In addition, congeners 101 and 92+84 were approximately twice the relative concentration as in the other traps. The major component of 31+28 returns in TSM samples T9 to T11. They are displaced in the PCA due to relatively low (approximately one-half) concentrations of 101, 74, and 70+76. Congener 66 was also very different, with the lowest value in T11. The magnitude of the differences in congener distributions among traps 8 to 11 and 1 to 5 imply that there were some real differences that are not attributable to the RPD.

The congener distribution in the first two SPM samples (P1 and P2) were similar to the sediments (Fig. 3). However, there is a significant change in the factor scores for P3 and P4 (Dec 1997 and May 1998, respectively). This is due to a two to three times higher concentration of congener 180 in these two samples, along with a four to five times higher relative concentration of 85 and 187+182. These concentrations are far greater than expected based on the RPD values than for these congeners in the sediments. Elevated concentrations of these congeners were never observed in any of the trap or sediment samples. Their source must be from outside the region of any local sediment resuspension, and they must be associated with slowly settling particles or they would have appeared in traps T10 and T11. No TSM sample was available from December 1997 for comparison. The final SPM sample (P5) was intermediate between the other four samples.

Particle composition influences

The particles in the different pools, surface sediment, TSM, and SPM, differ in composition including features such as particle size distribution, OC content, the source of the organic matter, and the extent of diagenesis of the organic matter. The SPM is likely the freshest material consisting of settling algae, zooplankton fecal pellets, and some resuspended particles. These particles have the highest OC content, and this material has undergone the least amount of diagenesis. Surficial sediments contain recalcitrant material of a range of sizes, including sand, and thus are expected to have the greatest range of characteristics. Trapped settling materials are intermediate, being composed of a mixture of suspended and resuspended materials. The differences in the characteristics are likely partly responsible for the observed differences in the partitioning behavior or the different sources [8,9].

Changes in partitioning among sediment types could be due to differences in OC composition or content among the particles. Suspended particulate material has the highest OC content and corresponding highest PCB concentration on a dry weight basis. Variation in contaminant partitioning has been observed in the laboratory using the polycyclic aromatic hydrocarbons phenanthrene, fluoranthene, and PCBs [33–35], resulting in variation in the partitioning behavior of nonpolar contaminants. Several recent studies have identified black or soot carbon content as a feature-enhancing partitioning [9,36]. Although soot carbon was not specifically measured for the present study, it was measured from a subsequent sediment collection from this site and found to be 0.03% of dry weight or 7.3% of the OC content [37].

Particle size differences between SPM and sediment may be a factor. Experimental data show that, as particle size decreases, time-to-equilibrium partitioning between water and particle phases also decreases [35,37]. Differences among particle sources also may affect the seasonal distribution of particles throughout the water column. Under unstratified conditions, there can be a substantial amount of sediment resuspension into the water column. Under summer stratification, sediment resuspension is lower. Thus, for TSM, the time of year and conditions of the water column may well dictate the composition of particles in the TSM pool. Further, the amount of primary productivity has a clear seasonal cycle, with a spring diatom bloom and a smaller fall bloom after overturn. Thus, the amount of fresh material contributing to the total trap particles could be substantial in the spring and early summer. This is supported by the amount of biogenic silica found in the May to July period, suggesting that settling diatoms, algae, and zooplankton fecal pellets are major contributors to the particle composition.

CONCLUSION

The concentration and congener distribution of PCBs in surface sediments, collected over a 14-month period, were constant (within analytical precision), even though there was seasonal and interannual variability of PCBs in SPM and TSM at the site. Potential causes of this inconsistency are particle sorting during sediment resuspension, seasonal changes in transient material (OC, SiO_2) on the particles (attenuated in the sediments), or the advection of particles from another source past the sampling site. Changes in the particle PCB congener distribution also could result from the same causes. A series of major storms in winter and spring 1998 could have remobilized PCBs from temporary sediment reservoirs that had not been disturbed for some time.

REFERENCES

1. Safe S. 1993. Toxicology, structure-function relationship, and human and environmental impacts of polychlorinated biphenyls—progress and problems. *Environ Health Perspect* 100:259–268.
2. Eadie BJ, Robbins JA. 1987. The role of particulate matter in the movement of contaminants in the great lakes. In Hites R, Eisenreich S, eds, *Sources and Fates of Aquatic Pollutants.* American Chemical Society, Washington, DC, pp 319–364.
3. Di Toro DM, Zarba CS, Hansen DJ, Berry WJ, Swartz RC, Cowan

CE, Pavlou SP, Allen HE, Thomas NA, Paquin PR. 1991. Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. *Environ Toxicol Chem* 10:1541–1583.

4. Pickard SW, Yaksich SM, Irvien KN, McFarland VA. 2001. Bioaccumulation potential of sediment-associated polychlorinated biphenyls (PCBs) in Ashtabula Harbor, Ohio. *J Gt Lakes Res* 27: 44–59.

5. Persson NJ, Gustafsson O, Bucheli TD, Ishaq R, Næs K, Broman D. 2002. Soot-Carbon influenced distribution of PCDD/Fs in the marine environmental of Grenlandsfjords, Norway. *Environ Sci Technol* 36:4968–4974.

6. Butcher JB, Garvey EA, Bierman VJ Jr. 1998. Equilibrium partitioning of PCB congeners in the water column: Field measurements from the Hudson River. *Chemosphere* 36:3149–3166.

7. Gobas FAPC, Maclean LG. 2003. Sediment-water distribution of organic contaminants in aquatic ecosystems: The role of organic carbon mineralization. *Environ Sci Technol* 37:735–741.

8. Delle Site A. 2001. Factors affecting sorption of organic compounds in natural sorbent/water systems and sorption coefficients for selected pollutants. A review. *J Phys Chem Ref Data* 30:187–439.

9. Cornelissen G, Guslafsson O, Bucheli TD, Jonker MTO, Koelmens AA, Von Noord PCM. 2005. Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: mechanisms and consequences for distribution, bioaccumulation, and biodegradation. *Environ Sci Technol* 39:6881–6895.

10. Eadie BJ, Robbins JA. 2005. Composition and accumulation of Lake Michigan sediments. In Muniwar M, Edsall T, eds, *The State of Lake Michigan.* Taylor and Francis, Philadelphia, PA, USA, pp 89–111.

11. Pignatello JJ. 1989. Sorption dynamics of organic compounds in soils and sediments. In Sawhney BL, Brown K, eds, *Reactions and Movement of Organic Chemicals in Soils.* SSSA Special Publication 22. Soil Science Society of America, and American Society of Agronomy, Madison, WI, pp 45–80.

12. Simcik MF, Eisenreich SJ, Golden KA, Liu S-P, Lipiatou E, Swackhamer DL, Long DT. 1996. Atmospheric loading of polycyclic aromatic hydrocarbons to Lake Michigan as recorded in the sediments. *Environ Sci Technol* 30:3039–3046.

13. Wong CS, Sanders G, Engstrom DR, Long DT, Swackhamer DL, Eisenreich SJ. 1995. Accumulation, inventory, and diagenesis of chlorinated hydrocarbons in Lake Ontario sediments. *Environ Sci Technol* 29:2661–2672.

14. Hermanson MH, Christensen ER. 1991. Recent sedimentation in Lake Michigan. *J Gt Lakes Res* 17:33–50.

15. Bogdan JJ, Budd JW, Eadie BJ, Hornbuckle KC. 2002. The effect of a large resuspension event in southern Lake Michigan on the short-term cycling of organic contaminants. *J Gt Lakes Res* 28: 338–351.

16. Hawley N, Wang X, Brownawell B, Flood R. 1996. Resuspension of bottom sediments in Lake Ontario during the unstratified period, 1992–1993. *J Gt Lakes Res* 22:707–721.

17. Hornbuckle KC, Smith GL, Miller SM, Eadie BJ, Lansing MB. 2004. Magnitude and origin of polychlorinated biphenyl (PCB) and dichlorodiphenyltrichloroethand (DDT) compounds resuspended in southern Lake Michigan. *J Geophys Res* 109:5017–5017.

18. Baker JE, Eisenreich SJ, Eadie BJ. 1991. Sediment trap fluxes and benthic recycling of organic carbon, polycyclic aromatic hydrocarbons and polychlorobiphenyl congeners in Lake Superior. *Environ Sci Technol* 25:500–509.

19. Zang H, Eisenreich SJ, Franz TR, Baker JE, Offenberg JH. 1999.

20. Thomann RV, Connolly JP, Parkerton TF. 1992. An equilibrium model of organic chemical accumulation in aquatic food webs with sediment interaction. *Environ Toxicol Chem* 11:615–629.

21. Morrison HA, Gobas FAPC, Lazar R, Haffner GD. 1996. Development and verification of a bioaccumulation model for organic contaminants in benthic invertebrates. *Environ Sci Technol* 30:3377–3384.

22. Eadie BJ. 1997. Probing particle processes in Lake Michigan using sediment traps. *Water Air Soil Pollut* 99:133–139.

23. Muzzi RW, Eadie BJ. 2002. The design and performance of a sequencing sediment trap for lake research. *Mar Technol Soc J* 36:23–28.

24. Lee C, Hedges JI, Wakeham SG, Zhu N. 1992. Effectiveness of various treatments in retarding microbial activity in sediment trap material and their effects on the collection of swimmers. *Limnol Oceanogr* 37:117–130.

25. Evans MS, Eadie BJ, Glover RM. 1998. Sediment trap studies in southeastern Lake Michigan: Fecal pellet express or alternate pathways. *J Gt Lakes Res* 24:555–568.

26. Eadie BJ. 1995. Trap sample splitting (wet). In *Lake Michigan Mass Balance Study (LMMB) Methods Compendium,* Vol I. Great Lakes National Program Office, U.S. Environmental Protection Agency, Chicago, IL.

27. Krausse GL, Schelske CL, Davis CO. 1983. Comparison of three wet-alkaline methods of digestion of biogenic silica in water. *Freshw Biol* 13:73–81.

28. DeMaster DJ. 1981. The supply and accumulation of silica in the marine environment. *Geochim Cosmochim Acta* 45:1715–1732.

29. Van Hoof P, Hsieh J-L. 1997. Extraction and cleanup of sediments for semivolatile organics following the internal standard method. In *Lake Michigan Mass Balance Study (LMMB) Methods Compendium Volume 2*: *Organic and Mercury Sample Analysis Techniques.* EPA905-R-97-012b. Great Lakes National Program Office, U.S. Environmental Protection Agency, Chicago, IL.

30. Marti EA, Armstrong DE. 1993. Polychlorinated biphenyls in Lake Michigan tributaries. *J Gt Lakes Res* 16:396–405.

31. Van Hoof P, Hsieh J-L. 1997. Analysis of polychlorinated biphenyls and chlorinated pesticides by gas chromatography with electron capture detection. In *Lake Michigan Mass Balance Study (LMMB) Methods Compendium Volume 2*: *Organic and Mercury Sample Analysis Techniques.* EPA905-R-97-012b. Great Lakes National Program Office, U.S. Environmental Protection Agency, Chicago, IL.

32. Chambers RL, Eadie BJ. 1981. Nepheloid and suspended particulate matter in southeastern Lake Michigan. *Sedimentology* 28: 439–447.

33. Huang W, Weber WJ Jr. 1997. A distributed reactivity model for sorption by soils and sediments. 10. Relationships between desorption, hysteresis, and the chemical characteristics of organic domains. *Environ Sci Technol* 31:2562–2569.

34. Brannon JM, Pennington JC, McFarland VA, Hayes C. 1995. The effects of sediment contact time on K_{OC} of nonpolar organic contaminants. *Chemosphere* 31:3465–3473.

35. Luthy RG, Aiken GR, Brusseau ML, Cunningham SD, Gschwend PM, Pignatello JJ, Reinhard M, Traina SJ, Weber WJ Jr, Westall JC. 1997. Sequestration of HOC by geosorbents. *Environ Sci Technol* 31:3341–3347.

36. Jonker MTO, Koelmans AA. 2002. Sorption of polycyclic aromatic hydrocarbons and polychlorinated biphenyls to soot and soot-like materials in the aqueous environment: Mechanistic considerations. *Environ Sci Technol* 36:3725–3734.

37. Kukkonen JVK, Landrum PF, Mitra S, Gossiaux DC, Gunnarson J, Weston D. 2003. Sediment characteristics affecting the desorption kinetics of select PAH and PCB congeners for seven laboratory-spiked sediments. *Environ Sci Technol* 37:4656–4663.

Evidence for increased gaseous PCB fluxes to Lake Michigan from Chicago. *Environ Sci Technol* 2129–2137.

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Newman MC. 2008. ''What Exactly Are You Inferring?'' A Closer Look at Hypothesis Testing. *Environ Toxicol Chem* 27:1013–1019.

The paper contained two block quotes in text. Only one block quote was set as such. The second block quote can be found on page 1015, second column. It reads:

> Awareness of the origins of the [null] ritual and of its rejection could cause a virulent cognitive dissonance, in addition to dissonance with editors, reviewers, and dear colleagues. Suppression of conflicts and contradicting information is in the very nature of this social ritual [16].

This material is a quote from Gezgerernder [16] as cited in the original paper. Allen Press apologizes to the author for this error.

Robinson SD, Landrum PF, Van Hoof PL, Eadie BJ. 2008. Seasonal variation of polychlorinated biphenyl congeners in surficial sediment, trapped settling material, and suspended particulate material in Lake Michigan, USA. *Environ Toxicol Chem* 27:313–322.

Materials and Methods:

The software for the PCA analysis used Prostat Version 4, Poly Software International, Pearl River, NY 10965. Prior to the calculation, the congener data were all normalized to the sum of the 15 PCBs in each sample.

Results

Two of the major congeners (138 and 153) in the Arochlor mixture that are generally reported in other sediment studies did not pass the quality control for inclusion in this work. Congener 138 co-elutes with congener 163, and this pair failed the quality control for the blank in all three matrices. For congener 153, it co-elutes with both congeners 105 and 132. These co-eluting materials could not be quantified due to an interference that affected the baseline, which precluded accurate integration. Thus, while these congeners are clearly present in the field sediments and in the matrix-spiked sediment, their accurate concentrations could not be determined for this study.

Table 4

INT = Interference precluded quantification

Units for Total PCBs should be ng/g